STUDIES IN THE CONJUGATED SYSTEMS. THE CHLORINATION OF 1-PHENYL-3-METHYL-BUTADIENE-1,3

A THESIS

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BY

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J. E. N.

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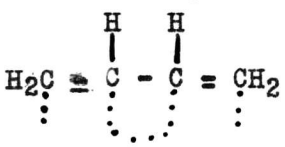
PART I

THEORETICAL

Numerous studies have been made concerning the addition of chlorine[1] and bromine[2] to butadiene to determine whether or not there is addition in the 1-2, or 1-4 positions. From certain studies in which chlorine[3] and bromine[4] add to butadiene in the 1-2 and 1-4 positions respectively, the relative amounts of isomers have been postulated to be determined by the nature of the solvent and the temperature at which the reaction is carried out.[5]

In 1899, the theory of partial valence[6] as postulated by Thiele was still being used to explain the addition of groups to the conjugated double bonds. It was thought in multiple linkage that the valence bonds did not utilize as much of the atomic affinity as was utilized in a single bond, leaving free a large, though variable, amount of affinity, partial valence.

In the case of butadiene-1,3, each of the four atoms would have a partial valence, represented by the following:



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1 Muskat and Huggins, J. Am. Chem. Soc., 51, 2496 (1929).

2 Straus, Berichte, 42, 2866 (1909).

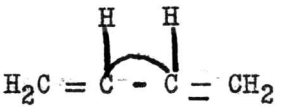
3 Farmer, Lawrence and Thorpe, J. Chem. Soc., 729 (1928).

4 Muskat and Northrup, J. Am. Chem. Soc., 52, 4043 (1930).

5 Hayes, Thedola, "The Bromination of 1-p-NitroPhenyl-2,3-Dimethyl Butadiene-1,3", (Unpublished Master's Thesis, Department of Chemistry, Atlanta University, 1952) p. 1.

6 Thiele, Ann., 87 (1899); ibid., 308, 333, (1899).

Two carbon atoms in the center are pictured as having free affinity, yet are bound together by a single bond; this affinity saturates itself across the single bond in a similar fashion, as shown below:



Additional reactions, therefore, take place on the first and fourth carbon atoms, the so-called 1-4 addition to conjugated systems.

Although Thiele's findings leave little room for doubt that he originally intended for his hypothesis to imply universal 1-4 addition to conjugated systems of double bonds, it has been long known that this position cannot be maintained, therefore, in the light of this kind of thinking, the Thiele hypothesis, even with later extensions, has not the diagnostic value which it was once intended to possess.[7] In other words, there exists no theory of orientation in additions to conjugated unsaturated systems comparable with the orientation theory which has developed for substitutions in aromatic systems.

Whereas Hayes[8] reports the addition of bromine to 1-p-nitrophenyl-2,3-dimethyl butadiene in the 1-4 position, it is the opinion of this investigator that the mode of addition of halogens depends upon the nature of the solvent and also the temperature at which the reaction is carried out. On this basis one might get addition in either or

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7 Burton and Ingold, J. Chem. Soc., 904 (1928).

8 Hayes, Thedola, op. cit., p. 1.

both positions. Hays[9] points out that the groups attached to the carbon atom will help determine the position at which addition will take place.

The equations listed represent the reactions that were carried out during this research.

1. $CH_3\ Br + Mg \longrightarrow CH_3\ Mg\ Br$

2. $C_6H_5 - \underset{H}{\overset{|}{C}} = \underset{H}{\overset{|}{C}} - \overset{O}{\overset{\|}{C}} - CH_3 + CH_3\ Mg\ Br \longrightarrow C_6H_5 - \underset{H}{\overset{|}{C}} = \underset{H}{\overset{|}{C}} - \underset{CH_3}{\overset{O\ MgBr}{\overset{/}{C}}} - CH_3$

I

3. $C_6H_5 - \underset{H}{\overset{|}{C}} = \underset{H}{\overset{|}{C}} - \underset{O\ Mg\ Br}{\overset{CH_3}{\overset{|}{C}}} - CH_3 + H_2O \xrightarrow{H_2SO_4} C_6H_5 - \underset{H}{\overset{|}{C}} = \underset{H}{\overset{|}{C}} - \underset{OH}{\overset{CH_3}{\overset{|}{C}}} - CH_3$

II

4. $C_6H_5 - \underset{H}{\overset{|}{C}} - \underset{}{\overset{|}{C}} = \underset{OH}{\overset{CH_3}{\overset{|}{C}}} - CH_3 \xrightarrow{H_2SO_4} C_6H_5 - \underset{H}{\overset{|}{C}} = \underset{H}{\overset{|}{C}} - \overset{CH_3}{\overset{|}{C}} = CH_2 + H_2O$

III

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[9] Hays, M. W., "Addition of Chlorine to 1-p-Nitrophenyl-2,3-dimethyl butadiene-1,3", (Unpublished Master's Thesis, Department of Chemistry, Atlanta University, 1954) p. 2.

Product II, was dehydrated by shaking with 30% sulfuric acid to give product III, 1-phenyl-3-methylbutadiene-1,3.

The qualitative tests were a negative for ketones and positive for unsaturation. A portion of the diene was chlorinated at zero degrees using carbon tetrachloride as the solvent.

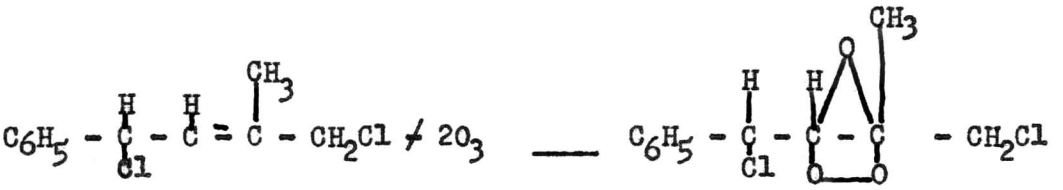
A saturated solution of chlorine in carbon tetrachloride was added dropwise to a carbon tetrachloride solution of the diene over a period of three and one half hours at which time the theoretical amount of chlorine had been added. The solvent was distilled from the dichloride at atomspheric pressure and the dichloride was distilled at one millimeter of pressure. The compound was analyzed immediately for chlorine. It was found that the amount of chlorine absorbed was that calculated on the assumption that a dichloride was formed. The dichloride on standing, slowly decomposed as indicated by the fact that it turned dark.

When the dichlorobutene was treated with a solution of sodium iodide in acetone and permitted to stand for twelve hours sodium chloride separated and iodine was liberated. The liberation of free iodine suggested that the chlorine in the compound was attached to adjacent carbon atoms.

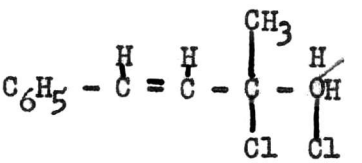
1. $C_6H_5-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}-\overset{CH_3}{\underset{Cl}{\overset{|}{C}}}-CH_2\,Cl + 2NaI \xrightarrow{\text{Acetone}} C_6H_5-\overset{H}{\underset{|}{C}}-\overset{H}{\underset{|}{C}}-\overset{CH_3}{\overset{|}{C}}-\underset{I}{CH_2} + I-$

2. $C_6H_5-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}-\overset{CH_3}{\overset{|}{C}}-\underset{I-}{\overset{I}{CH_2}} + I- \longrightarrow C_6H_5-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2 + I_2$

The results of the ozonolysis, however, indicated that the compound possessed the following structure:



Three dichlorides are theoretically possible depending upon whether 1-2, 3-4 or 1-4 addition takes place as indicated by the following equations:



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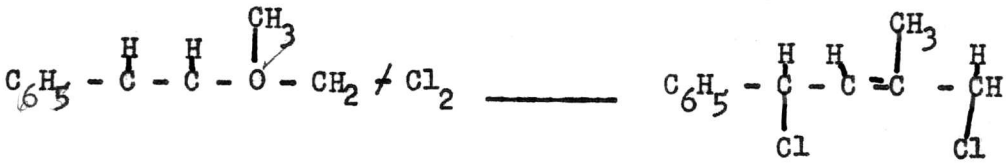

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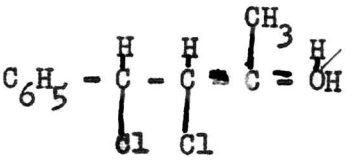


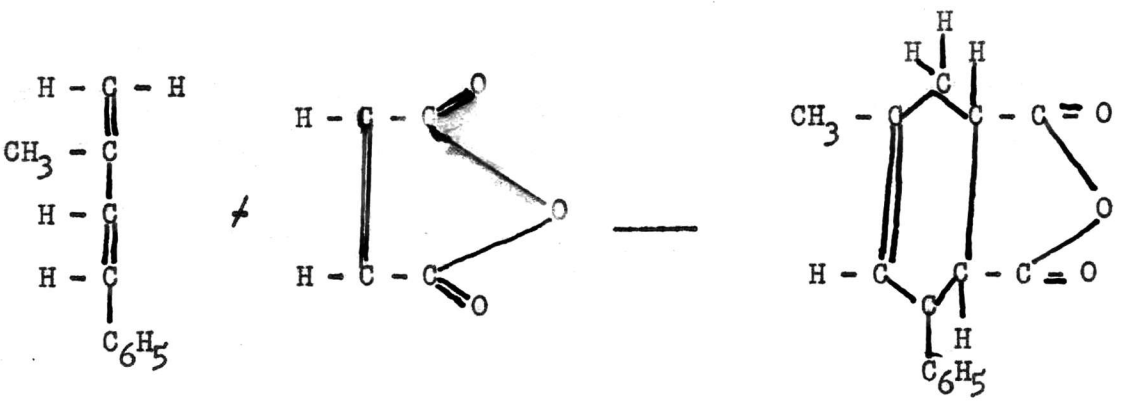
III

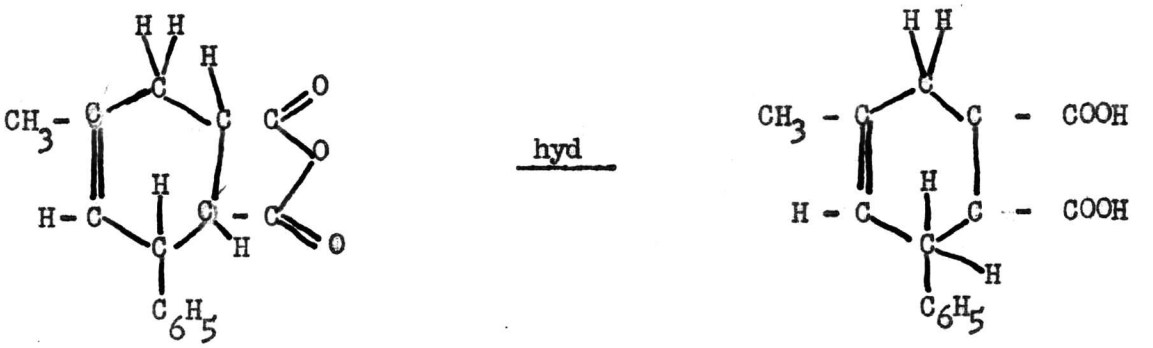
Compound I, would yield on ozonization and subsequent hydrolysis benzaldehyde and 2-methyl-2,3-dichloro propanal. Compound II would yield on ozonolysis alpha chlorophenyl acetic acid and alpha chloroacetone. Compound III would

yield on ozonolysis 4-phenyl-3-4-dichloro butanone-2 and formaldehyde. When the products of ozonolysis were worked up in the usual manner we were able to isolate alpha chlorophenylacetaldehyde as its 2,4-dinitrophenyl hydrazone derivative in 42% yield.

We were also able to isolate alpha chlorophenylacetic acid which was identified by a mixed melting point. Alpha chloroacetone was isolated in the form of its 2,4-dinitrophenyl hydrazone derivative. The isolation of these products indicated that the chlorine added to 1-phenyl-3-methyl-butadiene-1,3 in the 1-4 position.

A portion of the diene (III), was used to prepare a Diels and Alder derivative of which the neutralization equivalent was determined and found to be almost identical with the theoretical. The following equations represent the reactions involved:





The determinations of carbon, hydrogen and chlorine were within experimental error.

PART II

EXPERIMENTAL

The Preparation of 1-Phenyl-3-Methyl-Butadiene 1,3.[11]--In a three necked round bottom flask, fixed with a mechanical stirrer and a reflux condenser, was put 100g of methyl bromide, 20g of magnesium and 92g of benzalacetone in the presence of sodium dry ether. The methyl bromide was introduced into the reaction vessel, which contained the magnesium to start the reaction. Then the benzalacetone in ether was added dropwise and stirred continuously for one hour. The reaction mixture was allowed to stand for twenty four hours and dehydrated with a 30% solution of sulfuric acid. The etheral solution was washed several times with small portions of water. The ethereal solution was allowed to stand over night and dried over anhydrous sodium sulfate. The ether was distilled off at atmospheric pressure and the diene distilled at $72^{\circ}/2mm$. The diene, being a colorless oil, was weighed and 52.1g were obtained (a 57% yield). The qualitative tests were made and showed positive for unsaturation and negative for ketone.

The Maleic Anhydride Derivative.--One gram of the diene was dissolved in 50cc of thiophene free benzene and the mixture was poured into a (Kjeldahl) flask containing 1g of maleic anhydride and refluxed on a water bath for five hours. (The maleic anhydride and benzene were dissolved and filtered before adding the diene). Then it was hydrolyzed to the acid and titrated. The melting point of the derivative was 140°. The yield 0.9g was obtained (55%).

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[11] Klages, Berichte, 35, 2652 (1902).

Anal. Calcd for $C_{15}H_{16}O_4$: Neutralization Equivalent: 130

Found - Neutralization equivalent of 131.5 and 130.4

Molecular weight found: 263.0 and 260.8.

The Neutralization Equivalent.[12] The neutralization equivalent was calculated by the method given in footnote reference 12.

The Chlorination of 1-Phenyl-3-Methyl Butadiene.[13]--A saturated solution of chlorine in carbon tetrachloride (128ml, o.061g 1ml) was added to a solution of 16g (0.11 mole) of 1-phenyl-3-methyl butadiene in 200 ml of purified carbon tetrachloride. Throughout the addition which took 3.5 hours vigorous stirring was maintained while the temperature was kept near -20°C.

The product was washed several times with a 10% solution of sodium carbonate and then water in order to remove the excess acid. It was dried over night over anhydrous sodium sulfate. The dichloride distilled at 110° 1mm. It gave a positive Beilstien test. It was then analyzed for chlorine, carbon and hydrogen immediately. Six grams were obtained (a 25% yield), the rest polymerized.

Anal. Calcd. for $C_{11}H_{12}Cl_2$: C, 61.40; H, 5.58; Cl, 33.02.

Found C, 61.06, 59.31; H, 5.48, 5.36; Cl, 33.05; 34.99.

The Preparation of Chloroacetone.--Twenty-one grams of marble, broken into small pieces and 84g of acetone were placed in a flask provided with an inlet tube, dropping funnel and reflux condenser, and warmed to 40° in a water bath. A slow stream of chlorine was then passed in and enough water (a total of 50-60cc) slowly dropped in to keep in solution the calcium chloride formed

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12 Fuson and Shriner, "Identification of Organic Compounds", John Wiley and Sons, New York: (1948) p. 128.

13 Hellman, H., Hellman, W., and Mislow, K., J. Am. Chem. Soc., 76, 1175 (1954).

by interaction of the marble and hydrochloric acid. This was also aided by frequent agitation of the flask. The reaction must be carefully watched for if a yellow color develops, it indicates formation of hypochlorous acid and this if it accumulates, may react explosively with the acetone. In the event the solution turns yellow, the stream of chlorine is at once interrupted until the color disappears. When only a little marble is left, the reaction is discontinued, for although a large excess of acetone is present, the main product would be the symmetrical dichloro derivative $ClCH_2COCH_2Cl$, if this excess were not maintained. The mixture was allowed to stand at 40° until the evolution of carbon dioxide ceased making sure that an excess of marble was present, and was then poured off the marble into a separatory funnel. The two layers formed were separated and the lower layer consisting of a strong aqueous solution of calcium chloride was discarded.

The upper layer of acetone and its chlorination products were fractionated, monochloracetone boiling at 58-60° 1mm. The yield was 16.8g (21%).

The Ozonolysis of the Dichloride.[14] Four grams of the dichlorophenyl butene were dissolved in methylene chloride and a suitable amount of ozonized oxygen was bubbled through the solution until the oxidation was complete to test with potassium iodide starch paper. After the removal of the methylene chloride under reduced pressure of the water pump, the ozonide was decomposed with water. To assure complete decomposition, the solution was warmed on a water bath for four hours. The mixture consisted of an acid and a ketone, namely alpha chlorophenyl acetic acid and chloroacetone. The chloroacetone

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[14] Morris McDuffie, "Reduction of 1 Para Methoxy Phenyl Butadiene 1,3", (Unpublished Master's Thesis, Department of Chemistry, Atlanta University, 1952) p. 13.

was separated from the solution immediately and used to make the 2,4-dinitrophenyl hydrazine derivative which melted at 118 to 120°, the same as that prepared from authentic chloroacetone. When this derivative was mixed with the 2,4-dinitrophenylhydrazone prepared from known chloroacetone the mixture melted at 120°, Chloroacetone 1.4 was removed (a 93% yield). The acid being a solid was filtered off and identified as alpha chlorophenylacetic acid which melted at 58°. The acid weighed 1.9g representing a 73% yield calculated on the basis of the dichloride used.

The Preparation of the Chloroacetone Derivative from 2,4-Dinitrophenylhydrazine.[15] One gram of the ketone was dissolved in the minimum amount of methanol. It was treated at room temperature with freshly prepared Brady's reagent containing one mole of 2,4-dinitrophenylhydrazine. Per gram of 2,4-dinitrophenylhydrazine, 2ml of concentrated sulfuric acid, 15 ml of methanol and 5 ml of water were used. The precipitate of hydrazone was filtered within 5 to 10 minutes, washed well with cold aqueous methanol, dried, and recrystallized from a mixture of cold water and methanol.

The Preparation of Alpha Chlorophenylacetic Acid.[16] Four grams of dl mandelic acid were refluxed at 140° with 15 g of phosphorous pentachloride for four hours and the reaction mixture was distilled at 120°/27mm. Then the distillate was hydrolyzed with water to produce the acid which melted at 58°. A melting point was taken of a mixture of known alpha chlorophenylacetic acid and the acid obtained from the ozonolysis was also 58°.

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15 Fausto Ramirez and Arthur F. Kirby, J. Am. Chem. Soc., 74, 4333 (1952).

16 Walden, Berichte, 28, 1295 (1895).

SUMMARY

1. 1-Phenyl-3-methylbutadiene-1,3 was prepared by the dehydration of the carbinol obtained by the action of methylmagnesium bromine on 4-phenyl-3-buten-2-one.

2. The 1-phenyl-3-methylbutadiene reacted with maleic anhydride to give a solid Diels and Alder derivative which was identified by its melting point and its neutralization equivalent.

3. 1-Phenyl-3-methylbutadiene-1,3 reacts with chlorine to yield a 1,4 dichlorobutene.

4. The structure of the dichloro compound was determined by ozonolysis.

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